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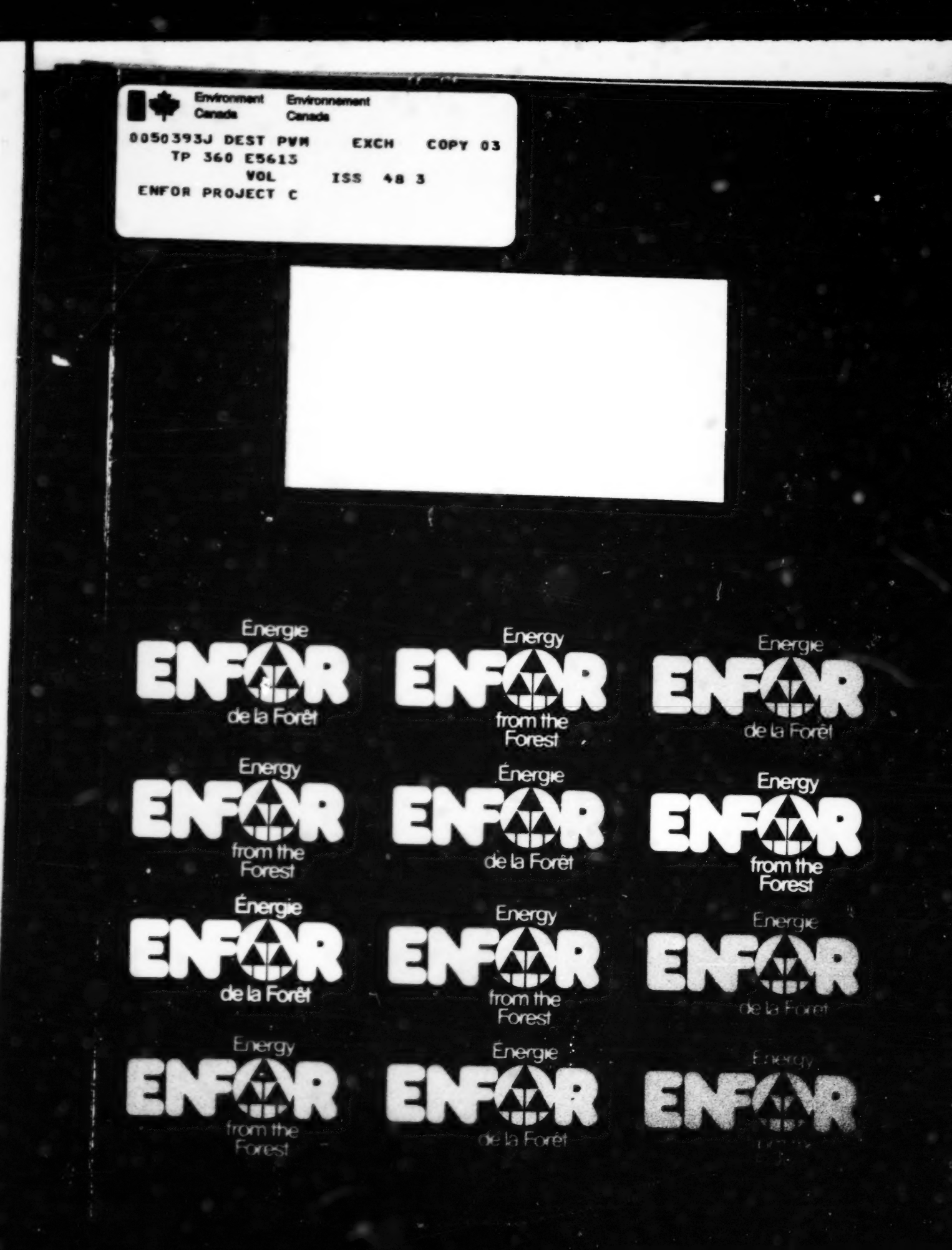

Contractor's Final Report [1/]
DSS Contract 24SU.KN107-2-4070

ENFOR Project C-48(3)

Production of Liquid Fuels and Chemicals from Lignocellulosic (Aspen) Materials

by

R.L. Eager, J.F. Mathews and J.M. Pepper

Contractor: University of Saskatchewan
Saskatoon, Saskatchewan
S7N 0W0

Scientific Authority:

Mr. R.J. Neale
Canadian Forestry Service
Environment Canada
11th Floor, Place Vincent Massey
Hull, Quebec
K1A 1G5

Technical Liaison Officer:

Dr. J.F.G. Mackay
Research Scientist, Energy from Wood Waste
FORINTEK Canada Corp.
Western Laboratory
6620 N.W. Marine Drive
Vancouver, B.C.
V6T 1X2

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ABSTRACT

Studies have been continued on the use of the small-scale semi-continuous reactor whereby lignocellulosic materials may be converted into a fuel oil. Changes in design and operation were made and further data obtained as a result of studies of the following parameters: pretreatment with sulfuric acid, operating pressure, presence or absence of CO, nature of feedstock.

The major study has centered around the design, construction and testing of a small-scale continuous reactor whose operation was based upon the use of a newly designed screw unit to compress and deliver the wood meal to the reactor site. Several successful runs were made using this reactor for periods up to six hours duration. The product oil was similar to that obtained previously using the semi-continuous reactor.

Chemical studies on oils obtained from both wood and cellulose (batch process) have been continued. A significant difference was noted between oils obtained from batch and continuous processes which are believed due to marked differences in reaction times at elevated temperatures. Some suggestions regarding the mechanism of formation of the chemical products are made.

Studies have been initiated to upgrade the wood oil to produce a higher quality gasoline-like fuel. These have involved the preparation and use of substantial quantities of the zeolite catalyst HZSM-5. Significant yields of C_6-C_{10} aromatic hydrocarbons (gasoline range) have been obtained in preliminary runs in batch reactors. A suitable pump has been designed and constructed to perform packed bed experiments on contacting proto-oil with HZSM-5.

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INTRODUCTION

This report deals with the results of the continuation of research conducted under ENFOR PROJECT NO C-48, DSS Contract No. OSS80-00234 (1981-82), for which a final report was submitted in July 1982. The conclusion reached from that research and recorded in the final report formed the basis upon which the continuing study was made. These conclusions were partially summarized in the Abstract.

Studies have been continued on the use of a small-scale semi-continuous reactor whereby aspen poplar wood meal may be converted into a fuel oil. Significant changes have been made in the design and operation of the unit resulting in increased throughput at lower pressures. Based on the new data consideration will be given to the design of a fully continuous reactor.

The relatively small amount of char that is formed in using the semi- continuous reactor appears to be only the result of start-up operations.

Further studies using the batch reactor have been made to evaluate the catalytic role of sodium hydroxide, lithium carbonate and cesium carbonate.

Detailed analysis of the oil obtained, by the batch process, from wood or from its separate components (cellulose and lignin) reveals a marked similarity of products. From these oils several alkanes, alkyl-substituted phenols and alkyl-substituted cyclopentanones have been isolated and identified.

RESEARCH OBJECTIVES

Based on the earlier results the research objectives to be considered under Contract No. DSU82-00008 were:

1. Determine the operating characteristics of a fully continuous, solid-feed reactor for the production of "proto-oil".
2. Continue the catalytic upgrading work with H-ZSM-5 and other commercial cracking catalysts.
3. Cooperate in the common feed-stock study initiated under the International Energy Agency.

EXPERIMENTAL PROCEDURES AND RESULTS

The design, construction and testing of a continuous reactor occupied most of the time covered by this report. During this interval experiments were continued on the liquefaction of biomass using the semi-continuous reactor.

A. Experiments using the semi-continuous reactor

a) Modification of the semi-continuous reactor

To allow the addition of reagents, such as an H_2SO_4 solution, to the wood meal before it entered the reaction zone an additional port, the "pretreatment port", was added to the reactor tube, see Figure 1. This port was located 14 cm downstream from the flange connecting the feed storage buffer to the reactor tube.

b) Wood meal

A new supply of wood meal was prepared. The aspen logs were first run through a planing mill. The resulting shavings were then passed through a hammer mill to yield a meal which would pass through a 1/32 in. mesh screen.

c) Pretreatment with sulfuric acid solution

At the Liquefaction Meeting in Saskatoon on February 16 and 17, 1982, the partial hydrolysis of wood with H_2SO_4 was discussed[1]. A series of experiments was made subsequently in which a H_2SO_4 solution was added to the wood meal prior to it coming into contact with a Na_2CO_3 solution. In the first of these experiments, runs 128 - 137, a H_2SO_4 solution, or in some cases distilled water, was pumped into the reactor through port A. In these experiments it was found that as a result of the presence of water the wood meal swelled and in several of the runs this resulted in stalling of the auger motor. It was for this reason that the pretreatment port was installed.

Concentrations of from 0.5M to 0.005M H_2SO_4 solutions were used at flow rates of approximately 8 mL/min. In Table 1 are shown the results of a comparison using ^{13}C-NMR between oil samples prepared using different concentrations of H_2SO_4 under similar conditions, 360°C, 21-24.5 MPa, auger speed of 12 rpm, and 5% Na_2CO_3 at a flow rate of 8 mL per min. In a study of the water content of oil samples (see later) some oils were included which had been prepared using a H_2SO_4 pretreatment, the results are given in Table 2. The properties of the oils prepared in these runs did not appear to be markedly different than those prepared in similar runs where no H_2SO_4 pretreatment was used.

d) Effect of operating pressure

The operating pressure used directly affects the capital costs of a commercial plant. It was therefore of considerable interest to determine how low the operating pressure could be without markedly affecting the properties of the oil. A series of runs were made in each of which the operating pressure was maintained at a desired value by a suitable balance between the rate of addition of CO and rate at which gases were vented from the reactor. A summary

of the results obtained is presented in Table 3. The results indicate that oil can be satisfactorily produced at reactor pressures as low as 14 MPa. At 10.5 MPa it was not possible to maintain the temperature at 360°C, presumably due to an increased rate of evaporation of water. As the pressure is reduced from 24.5 MPa it is found that more heat energy is required and at 10.5 MPa the capacity of the electric heaters was not sufficient to maintain a temperature of 360°C. Too low a temperature results in char or a black powdery product. Furthermore it has also been found that if the reaction mixture is low in water a similar product is formed. However it has not been proven that pressures as low as 10.5 MPa are not suitable. Mechanical problems have delayed a proper inspection of this low pressure region.

e) Effect of presence or absence of CO

Earlier experiments with the batch reactor had indicated that in experiments in which N_2 was used instead of CO oil would be produced in yields and with analysis similar to that produced in experiments where CO was present. Two runs were made with the semi-continuous reactor in which the reactor was originally pressurized with N_2 and in which no CO or N_2 was added during the run. The results together with those from control runs using CO are given in Table 4. It would appear that there is no advantage to be gained by using CO. It should also be recalled that previous experiments indicated no difference when H_2 or CO were used.[2] These results have significant implications in the economics of a commercial process.

f) Use of cellulose and spruce wood as feed stock

Cellulose is one of the model compounds used in previously reported batch reactor studies. It was of interest to determine if oil could be produced from cellulose in the semi-continuous reactor. Since spruce is an abundant soft wood it was decided to also attempt the preparation of oil from spruce wood

meal. With both of these materials difficulty was experienced in forming a plug. For both it was necessary to use operating pressures higher than those necessary for poplar wood meal. For both cellulose and spruce wood an oil was prepared. A summary of the results are given in Table 5.

g) Examination of the aqueous phase

The aqueous phase from two runs was analyzed by a procedure similar to that reported elsewhere[3]. The reactor conditions to produce the aqueous phase were: temperature, 360°C; pressure, 21 MPa; Na_2CO_3 solution, 5%; feed rate, 6 mL/min. In both runs it was not possible to establish a pressure plug and the runs were stopped after 0.75 hr. An outline of the analytical procedure used is as follows:

The yields of the various fractions, based on weight of wood meal, are as follows:

Oil Yield	32.1%
Fraction A	1.21
Fraction B	4.01
Fraction C	6.88
Fraction D	8.00
Fraction E	6.83

No attempt was made to determine the mass of water produced. Fraction E was found to contain 41.2% C and 6.2% H, which suggests it is still essentially carbohydrate degradation products. These yields represent a distribution of products that is quite different to that reported as a result of a similar fractionation of the aqueous layer from a reaction run in the batch reactor[3]. This represents an important difference between the batch and continuous processes and is likely due to the significant different in residence time at elevated temperatures.

B. Experiments using the batch reactor

Two substrates other than poplar wood were used, namely Saskatchewan peat moss and milk weed. The milk weed material was air-dried whole above-ground plant. In each run the conditions were: substrate, 100g; water, 500 mL; Na_2CO_3, 10 g; initial CO pressure, 3.5 MPa; final temperature, 360°C for 1 hr.

The product from the peat moss was a heterogeneous mixture of sticky tar and char together with an aqueous phase containing a suspension of material thought to be inorganic. The yield of the heterogeneous mixture was 39%, containing 75.7% C, 8.3% H and 1.7% N.

The product from the milk weed was a heterogeneous mixture of black tar and an insoluble solid. The yield was 22.3% containing 67.6% C, 8.1% H and 2.9% N. Upon extraction with acetone an 18.3% yield, based on original milk weed, of an oil was obtained, 79.3% C, 9.0% H and 3.6% N together with a 4.0% yield of an insoluble solid, 15.0% C, 1.9% H and 0.5% N.

C. Water content of the wood oils

As a result of discussions on oil analysis during the February 1982 meeting in Saskatoon[1] it was decided to establish a method for determination of the water content of the oils being produced. The method finally developed was to first centrifuge an oil sample, decant off the water which separated, and then determine the water content of the remaining oil sample by the Karl Fischer method. Titration of the original oil did not lead to consistent results, presumably because the water was not uniformly distributed through the oil.

Values found for the water contents of oils produced in the semi-continuous reactor showed a range from 10% to 20%. Some of the results from the studies of the water content of oils are presented in Table 2. The oil yield values reported for the semi-continuous reactor runs have not been corrected for the water content of the oil; in many cases oil samples are no longer available. The oil yield values for the continuous reactor studies, to be reported upon later in this report, have been corrected for their water content. The reported values for the percentage of carbon and hydrogen will not be greatly affected since the small samples required for the C-H-N analyzer have always been air-dried and tests indicated the presence of a maximum of 4% water in the resulting samples.

Some typical batch runs were made and the water contents of the resulting oils were determined. In these runs a value of 12% water was found. It would thus appear that the yields reported earlier for the batch runs are not seriously in error.

D. The continuous reactor

a) Construction and testing

In the early planning stages, in consultation with Mr. G. Dyck of the Engineering Shops, University of Saskatchewan, it was decided to use a new screw design as the essential part of a feeder unit. The new screw would deliver compressed wood meal to the reactor auger. The reactor auger would be basically of the same design as the auger used in the semi-continuous reactor. The seal "plug" would be formed on the feeder screw with the reaction resulting in oil production occurring in as short a space as possible following the seal. No plug formation would be required on the reactor auger, in fact such a plug would be undesirable. Since the reaction has been found to occur very rapidly the reactor tube and auger could be shorter than the one used in the semi-continuous reactor.

In order to obtain some idea of the problems involved a proto-type feeder was constructed. It was tested on a lathe bed, using the lathe motor to drive the screw. The feeder successfully handled poplar wood meal. The unit was pressure tested using compressed nitrogen from a cylinder, the feeder was able to feed wood meal against a pressure of 14 MPa. The major problem was the high feed rate, approximately 34 g of wood meal per min. This high feed rate was undesirable for several reasons:

1) The amount of wood required would have posed a problem.
2) The electric heaters currently available could not supply the energy required to heat and evaporate the water which would be needed.
3) The motor size required to run the screw would have necessitated the purchase of an unduly expensive motor.

Another feeder with a smaller capacity was constructed. This feeder was provided with an electric motor so as to form a self-contained unit. The compressed wood meal leaves the feeder in the form of a close spiral with a hollow center. Fig. 2 is a close-up photograph of the feeder in operation whereas Fig. 3 shows a length of the extruded material which was allowed to slide over a metal rod for support. The following are some typical results of feeding tests:

Bulk density of original wood meal	0.14 g/mL
Density of extruded compressed wood meal	1.3 g/mL
Mass per unit length of spiral	0.97 g/cm
Feed rate of wood meal at 14 rpm	9.9 g/min

The density of the extruded material was found both by the liquid displacement method and also by the sink-and-float method using mixtures of CCl_4 and CH_3OH of known density.

The feed rate of 9.9 g/min was approximately one third of the proto-type feeder but it was three times greater than that of the semi-continuous reactor. Consequently the ability to supply sufficient heat and water remained a problem. As a result it was decided to reduce the feeder auger speed from 14 to 7 rpm and also to supply part of the water as high pressure steam. These

modifications were found to be workable and it was decided to start experimental work with this version of the continuous reactor, which is described in more detail in the following section.

b) Details of the continuous reactor

A schematic of the continuous reactor is shown in Fig. 4. The portion to the right of section J-J is part of the original semi-continuous reactor and was described previously[4]. The continuous feeder unit consists of a hardened 316 tool steel housing into which is fitted a tool steel screw driven by a 1/2 HP motor coupled to a speed reduction gear box and a set of pulleys and a V-belt. The set of pulleys which are in use give a screw rotation speed of 7 rpm.

To prevent torque being developed which could result in damage to the equipment an automatic shutoff was added. An arm, the "torque arm" is attached to the feeder unit housing which is free to rotate. The end of the torque arm bears against a spring loaded plate which in turn can contact a micro-switch and result in the electric circuit supplying current to the motor being opened. This unit is set to shut the reactor down when the torque reaches a value of 160 N-m.

In preliminary testing it was found that sufficient heat was generated in the feeder unit to raise the temperature of the feed to approximately 90°C. It was also found that to be able to start the unit its temperature had to be in the 40-70°C temperature range. In order to be able to either heat or cool the feeder housing both the housing and the torque arm were provided with passages drilled in them and fitted with connectors so that cooling water, or warm water, could be directed through them. Heating could also be provided by a heating tape wrapped around the feeder unit housing.

A hopper, constructed of acrylic plastic, is used to contain a supply of wood meal. At the bottom of the hopper a screw with the ends having opposed pitches feeds the wood meal into the center of the hopper bottom where an opening allows the meal to drop onto the feeder screw. The hopper screw is driven by a small electric motor coupled to a speed reduction box through a pair of belt driven pulleys.

The auger in the reactor tube is threaded at the end nearest the feeder unit and screws onto the end of the feeder unit screw. Hence the 1/2 HP motor drives both the feed unit screw and the auger in the reactor tube.

The feeder unit must initially be loaded with wood meal without any back pressure in order to be able to form a plug and without unreacted wood accumulating in the reactor tube. To accomplish this the following start-up procedure is used. The reactor tube and auger are removed from the feeder unit. The hopper is filled with wood meal, the feeder housing heated to 40-70^{o}C and the feeder unit started. The feeder unit is run for a sufficient length of time, approximately 15 minutes, until wood meal appears at the exit end of the feeder unit. The feeder unit is now filled with a solid core of wood meal which is capable of resisting the back pressure which will be developed in the reactor tube. The auger is screwed into the end of the feeder unit screw and the reactor tube slipped over the auger and attached to the feeder unit.

c) Operation of the continuous reactor

In a typical run the reactor was initially pressured to 13.6 MPa with CO and the feeder unit housing was heated to 40-70^{o}C by use of a heating tape. The flow of the Na_2CO_3 solution, the flow of steam and the motor driving the feeder unit and the auger were all started at the same time. A 10% Na_2CO_3

solution was pumped in at port B at the rate of 6 mL/min and steam was added at port A at the rate of 8 g/min. CO was added through port E and exhaust gases were removed through valve K in order to maintain the reactor at the desired operating pressure of 17.7 MPa. Once the unit was started the heating tape was removed from the feeder unit housing and sufficient cooling water was used to maintain the housing temperature in the 40-70°C range. The electric heater on the reactor wall between C and D was used to bring the reactant temperature to 360°C at D and the heaters between D and F were used to maintain 360°C in that region. Cooling water was run through the cooling sleeve on the downstream side in order to maintain the temperature at F at 125°C. Liquid product was removed from the bottom of collector H. At the end of 6 h it was decided to terminate the run. At that time the reactor was running smoothly and no difficulties were being experienced.

d) Results of operation of the continuous reactor

i) Typical run

In the run cited in part (c) a total of 1540 g of wood was fed to the reactor, the average feed rate being 4.28 g/min. A water-to-wood ratio of 3.3:1 and a Na_2CO_3-to-wood ratio of 0.15:1 were used. A total of 816 g of wet oil was collected which was found to contain 34.4% water. The result was therefore 535 g of dry oil which corresponded to a yield of 35% on a dry wood basis. An analysis of the oil showed 68.5% C and 6.7% H. The measured higher heat of combustion was 31.9 MJ/kg.

ii) Variation of operating parameters

Some work has been done to vary the operating parameters of the process. Water-to-wood ratios as low as 2.5:1 and Na_2CO_3-to-wood ratios as low as 0.0125:1 have been used successfully. Reactor pressures from 15 to 32 MPa have

proved operational with 32 MPa appearing to be the upper limit for the present screw-feeder design.

Nitrogen has been used to initially pressurize the reactor to 13.6 MPa; no CO was used in the reaction. This was a 6 h run, similar to that described in part (c) except that a water-to-wood ratio of 2.5:1 was used and the Na_2CO_3-to-wood ratio was dropped from 0.025:1 to 0.0125:1 at the ends of two hour intervals. For the total run 1593 g of wood meal had been fed to the reactor resulting in 667 g of dry oil or a yield of 42%. The product oil analysed 70.1% and 6.5% H.

E. Upgrading of wood oil

a) Catalyst Preparation

ZSM-5 catalyst was prepared according to methods reported in the patent literature[5,6]. The procedure involved the heating of a mixture containing appropriate amounts of sodium silicate solution, aluminum sulfate, propanol and ZSM-5 seed slurry in an autoclave at 175°C for 1-4 days. This step was followed by filtering, washing and calcining (in air at 400°C) of the resulting product. The H^+ form was prepared by acid leaching of the ZSM-5 using HCl. Each batch yields ca. 15 g of catalyst. The resulting HZSM-5 catalyst batches were analyzed for Al and Na contents using atomic absorption. A typical sample of HZSM-5 contained 1.72% Al and 0.083% Na. The HZSM-5 samples were also characterized by X-ray diffraction. The XRD patterns were compared to those reported in U.S. Patent 3,702,886[5] and showed only those peaks reported in the Patent. A crystallization time (at 175°C) of 24 h was choeen as optimum, based on the XRD analyses of various samples.

b) Batch Reactor Runs

Three preliminary runs involving the contacting of proto-oil with HZSM-5 catalyst were conducted in a 300 mL magnetically stirred autoclave. This autoclave has a maximum operating pressure of 17.2 MPa. Consequently difficulty was experienced, with the pressure reaching 13.8 MPa at 300°C whereas the effective operating temperature for HZSM-5 is above 350°C. In order to attain high temperatures the autoclave was vented when the pressure reached 13.8 MPa and the temperature was then raised to 400°C. The vented material consisted of gases, water, and an oil fraction. The gas fraction was analyzed and found to consist of methane, C_2, C_3 and C_4 alkanes and alkenes, CO and CO_2. The oil fraction was flash evaporated at a pressure of approximately 0.6 torr. The distillate consisted of aliphatic hydrocarbons, the majority being in the C_{12}-C_{18} range. The residue from the flash evaporation contained 82.9% C and 7.3% H. Approximately 43% of the original proto-oil remained in the autoclave in the form of a solid char containing 87.2% C and 2.0% H.

These preliminary results indicated that the catalyst does remove oxygen from the proto-oil (which originally contained approximately 20% oxygen) and that hydrocarbons are produced. The autoclave used is not very satisfactory for this work due to the pressure limitation. The venting of the gases at lower temperatures very likely resulted in the removal of all water present. Past experience indicates that the proto-oil is stable up to temperatures in excess of 360°C if water is present, but that in the absence of water charring occurs.

Another preliminary run has been made using the 1.4 liter vessel previously used in the batch work for the production of proto-oil. A mixture of 107 g wood oil, 300 mL of water, 3.5 MPa hydrogen, and 5 g of HZSM-5 catalyst was used. The vessel was heated to 400°C for 1 hour, during which time a maximum

pressure of 37 MPa was reached. When the vessel was cooled down there were present 43 g of an oil and char mixture.

The gas phase was analyzed and found to consist of methane, ethane, propane and C_4 hydrocarbons, only a very small quantity of alkenes were present.

The oil and char mixture was flash evaporated at 200°C and 1 torr pressure. Based on the mass of the oil and char mixture 18% flashed off as water and 15% as a distillate. This distillate showed gas chromatographic peaks characteristic of aromatic and aliphatic hydrocarbons. A sample of the original proto-oil was also flash evaporated. The distillate from the catalyst treated oil showed a higher aromatic hydrocarbon content than did that from the original oil.

c) Packed bed microreactor

A 1/4" S.S. microreactor is available for the evaluation of catalysts in fixed-bed configuration. However the piston pump which has been used is not suitable for pumping proto-oil. A new syringe-type positive displacement pump has been designed and constructed. With this new pump proto-oil will be contacted with HZSM-5 in this microreactor set-up.

F. Chemical studies on wood and cellulose oils[1]

A study of the chemical composition of the oil fraction obtained by the liquefaction of wood and cellulose has been continued. Capillary gas chromatographic - mass spectrometric analyses of fractions resulting from a silica gel column separation of the oils indicated the presence of higher molecular weight compounds than the phenols and cyclopentanones reported in last year's report. These compounds have been identified as various phenols, naphthols, cycloalkanols, cycloalkanones, polycyclic and long chain alkanes and alkenes[4].

Along with the relatively low molecular weight components, studies using both gel permeation and high-performance size exclusion chromatography have shown the presence of higher molecular weight (polymeric) substances with molecular weights up to 2000 but with a significant fraction of 400. Chemical degradations have revealed that linkages involved in these higher molecular weight fractions are of the oxygen-ether type, and that the repeating units are essentially phenolic.

A significant difference was noted in the composition of the oil obtained using the batch reactor (residence time of one hour at 360°C) on the one hand and that obtained using the semi-continuous reactor[(4)] (one minute at 360°C) on the other. In the latter case, less degradation of the products resulting from the lignin component was observed in that the resulting phenolic components retained the methoxyl substituents which were cleaved under the conditions of the batch process. If the liquefaction process were to become valuable as a source of chemicals then there is evidence for the advantages of the continuous (short residence time) method.

[1]Work performed by a post-graduate student, Mr. J. Roy - but financed by the ENFOR Contract only for materials and supplies.

Studies have been initiated towards an understanding of the mechanism(s) whereby wood components (cellulose, hemi-celluloses, and lignin) are converted into the chemicals found to comprise the oil fraction. Using cellulose as the feed material evidence has been obtained to support the concept that the liquefaction is a two-step process. As a result of a series of runs made under increasing temperatures (50, 100, 175, 200, 250, 300, 325, 360°C) it is apparent that initially an alkali-catalyzed degradation of the cellulose results in the production of a water-soluble (acidic) fraction which is subsequently further degraded under acidic conditions, to the resulting oil components.

Part of these studies have been accepted for publication[7].

G. Summary

The continued successful operation of the semi-continuous reactor to produce an oil from wood meal has firmly established the principle that a "plug" of wood meal can be produced to maintain a significant pressure differential between the wood hopper and the reactor zone. This principle has now been applied in the design, construction and successful operation of a continuous unit whereby wood meal may be introduced at atmospheric pressure into the reaction zone held at around 17.5 MPa pressure. This has been achieved by the use of a new screw unit which serves to both compress the wood meal into a plug which withstands the back pressure of the reactor zone and, as well, delivers the wood into the reactor. Several successful runs have been made using this continuous reactor for periods up to six hours duration. An oil is produced in yields of 35-42 percent (dry wood basis), which analyzes for C 68.5 - 70% and H, 6.7 - 6.5%, and has a measured higher heat of combustion of 32 MJ/kg. Not only has it been shown very feasible to operate on a continuous

basis, with the wood being introduced at atmospheric pressure but the reaction has been shown to be successful at a reactor pressure of only 17.5 MPa. Both of these observations are of great significance in terms of a commercial sized unit.

Although it is important to recognize that a functioning continuous unit has been made and tested whereby wood maybe converted into an alternate fuel, the chemical nature of this fuel may restrict its direct use to one similar to that of a Bunker fuel. The second major development of this study has been to show that the original oil may be upgraded significantly, using a zeolite-type catalyst, H-ZSM-5, to produce a spectrum of aromatic hydrocarbons in the C_6 to C_{10} range which in part or in whole are suitable components of a gasoline type fuel.

Further studies on the chemical composition of oils produced by the liquefaction of wood or its separate components, are leading to a better understanding of the mechanism of the complex processes involved. Such information will contribute to further improvements in the conversion process.

H. Publications

1. R.L. Eager, J.F. Mathews and J.M. Pepper. Conversion of Aspen Poplar into Liquid Fuel. In Specialists Meeting on Biomass Liquefaction, Saskatoon, February 1983, pp. 1-14.
2. R.L. Eager, J.F. Mathews and J.M. Pepper. Liquefaction of aspen poplar wood. Can. J. Chem. Eng. 60, 289-294, (1982).
3. R.L. Eager, J.F. Mathews, J.M. Pepper and H. Zohdi. Studies on the products from the conversion of aspen poplar to an oil. Can. J. Chem. 59, 2191-2198 (1981).
4. R.L. Eager, J.M. Pepper and J.F. Mathews. A small-scale semi-continuous reactor for the conversion of wood to fuel oil. Can. J. Chem. Eng. 61, 189-193 (1983).

5. U.S. Patent 3,702,886. R.J. Argauer and G.R. Landolt. Crystalline Zeolite ZSM-5 and method of preparing the same, November 1982.

6. U.S. Patent 4,175,114. C.J. Plank, E.J. Rosinski and M.K. Rubin. Method for Producing Zeolites. November 1979.

7. R.L. Eager, J.M. Pepper, J.C. Roy and J.F. Mathews. Chemical studies on oils derived from aspen poplar wood, cellulose and an isolated aspen poplar lignin. Can. J. Chem. 61, August (1983).

I. Acknowledgements

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TABLE 1

EFFECT OF PRETREATMENT WITH H_2SO_4

	% Aromaticity[1]	Other Difference
Run 95 No pretreatment of meal	50	Fluid oil
Run 129 0.5 M H_2SO_4	61	Emulsion of char and oil
Run 131[2] 0.05 M H_2SO_4 Top Layer	64	Emulsion of char and oil
Run 131[2] 0.05 M H_2SO_4 Botton Layer	46	Fluid Oil
Run 133 0.005 M H_2SO_4	50	Fluid Oil

[1] % aromaticity refers to all unsaturated carbons as seen by ^{13}C-NMR.

[2] The oil product in run 131 separated into two layers.

TABLE 2

WATER CONTENTS OF OILS

Run Number and Date Run[1]	Condition of the Run	Pretreatment Solution	Water Loss by Centrifuge	Water Content by Karl Fischer	Total Number Content
144 May 21/82	21 - 24.5 MPa 480 mLs/hr 5% Na_2CO_3 Auger speed 15 rpm 360°C	water 50 mLs/hr	6.3%	11.5%	17.1%
145 May 26/82	21 - 24.5 MPa 480 mLs/hr 5% Na_2CO_3 Auger speed 18 rpm 360°C	water 50 mLs/hr	6.9%	11.0%	17.2%
147 June 1/82	21 - 24.5 MPa 480 mLs/hr 5% Na_2CO_3 Auger speed 18 rpm 360°C	0.0005M H_2SO_4 50 mLs/hr	6.04%	12.4%	17.7%
148 June 3/82	14 - 17.5 MPa 480 mLs/hr 5% Na_2CO_3 Auger speed 15 rpm 360°C	0.0005M H_2SO_4 50 mLs/hr	7.6%	12.6%	19.2%

[1] It should be noted that the water content was determined on June 4/82 for all oil samples.

TABLE 3

EFFECT OF OPERATING PRESSURE[1]

Operating Pressure MPa	Duration of Run hr	Yield of Oil[2] %	%C	%H	Comments
24.1	2.50	41.0	69.7	7.1	Satisfactory operation
17.2	2.00	37.0	66.0	7.0	Satisfactory operation
13.8	2.25	37.0	67.8	6.7	Satisfactory operation
10.3	1.50	no oil black powder	67.2	6.7	Max temp. 340 - 345°C

1 Temperature, 360°C; auger speed, 15 - 17 rpm; Na_2CO_3 solution (5%) fed at 8 - 10 mL per min.

2 Calculated on a dry wood basis.

TABLE 4

COMPARISON OF PROPERTIES OF OIL PRODUCTS IN PRESENCE OR ABSENCE OF CO[1]

Run	Gas	Operating Pressure MPa	Yield of Oil[2] %	%C	%H	% Aromaticity[3] by ^{13}C-NMR	High Heat of Combusion KJ per kg
95	CO	20.7	42.0	76.2	6.7	50	------
96	N_2	20.7	41.0	69.5	7.0	56	------
149	CO	13.8	37.0	67.8	6.7	--	29,960
153	N_2	13.8	38.0	67.2	6.7	--	30,120

1 Temperature, 360°C; duration of run, 2.25 hrs.; Na_2CO_3 solution, 5% feed rate, 8 - 10 mL/hr.

2 Calculated on a dry wood basis.

3 Comparable determinations using oil samples produced in the batch reactor yield a value of 36% aromaticity.

TABLE 5

USE OF CELLULOSE AND SPRUCE WOOD MEAL AS FEEDSTOCK[1]

Run	Feedstock	Operating Pressure MPa	Duration of Run hr	Yield of Oil[2] %	%C	%H	Comments
138	Cellulose[3]	24.1	1.00	sticky emulsion of oil and char			No plug formed
146	Cellulose	29.7	1.00	34	68.4	6.2	a weak plug
158	Aspen	20.7	2.00	39.0	55	6.5	control run
160	Spruce	20.7	1.50	30.0	71.5	6.4	33g of char, plug not maintained
161	Spruce	34.5	2.25	36.0[4] 10.7[5]	73.5 73.1	6.8 6.9	continuous, very viscous oil

[1] Temperature, 360°C; auger speed, 12 rpm; Na_2CO_3 solution, 5%, feed rate 6 - 8 mL/min

[2] Based on mass of feedstock used.

[3] MN-Cellulose powder for column chromatography.

[4] Very viscous oil.

[5] A mixture of oil and char.

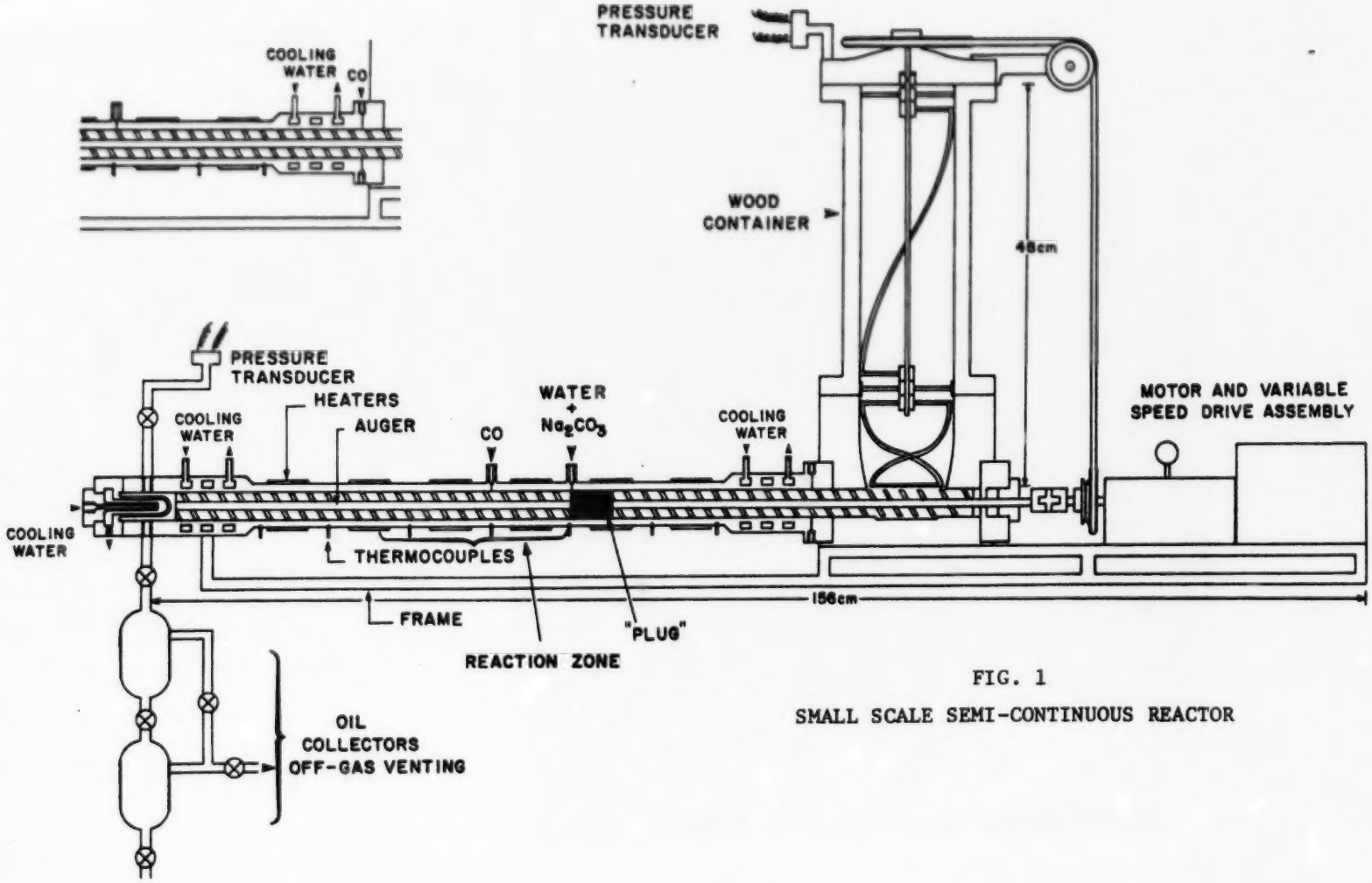

FIG. 1

SMALL SCALE SEMI-CONTINUOUS REACTOR

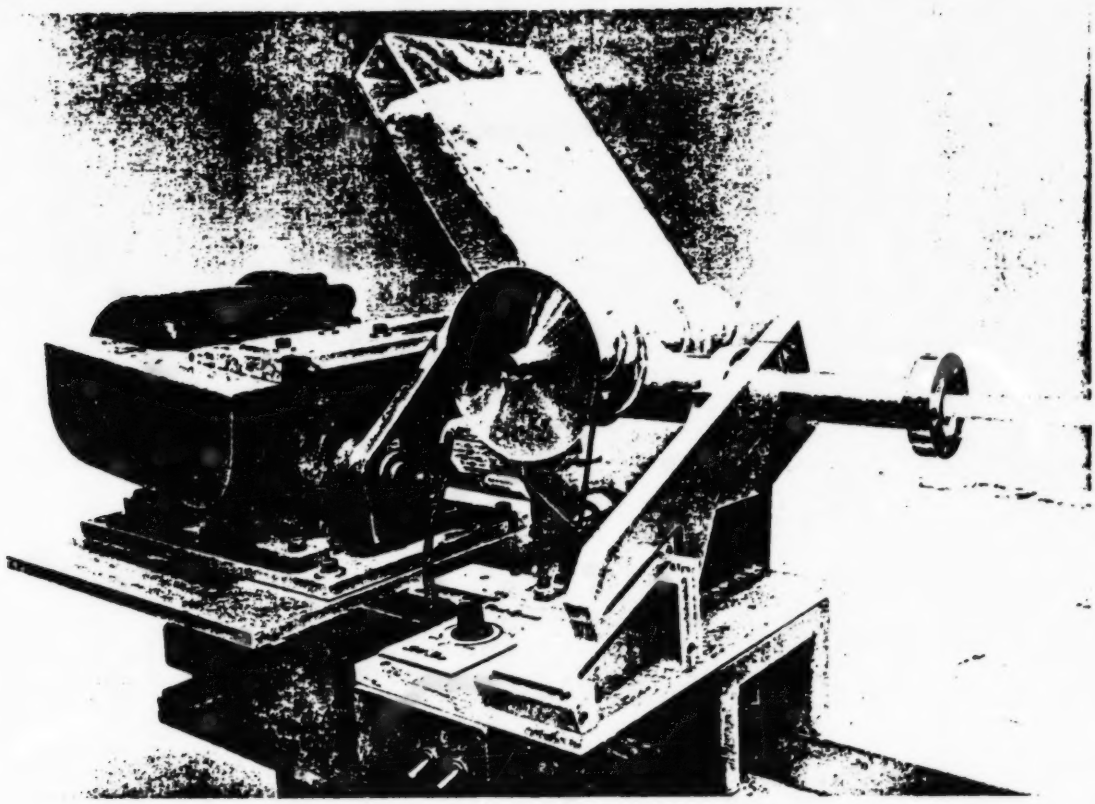

FIG. 2. WOOD MEAL FEEDER OF CONTINUOUS REACTOR

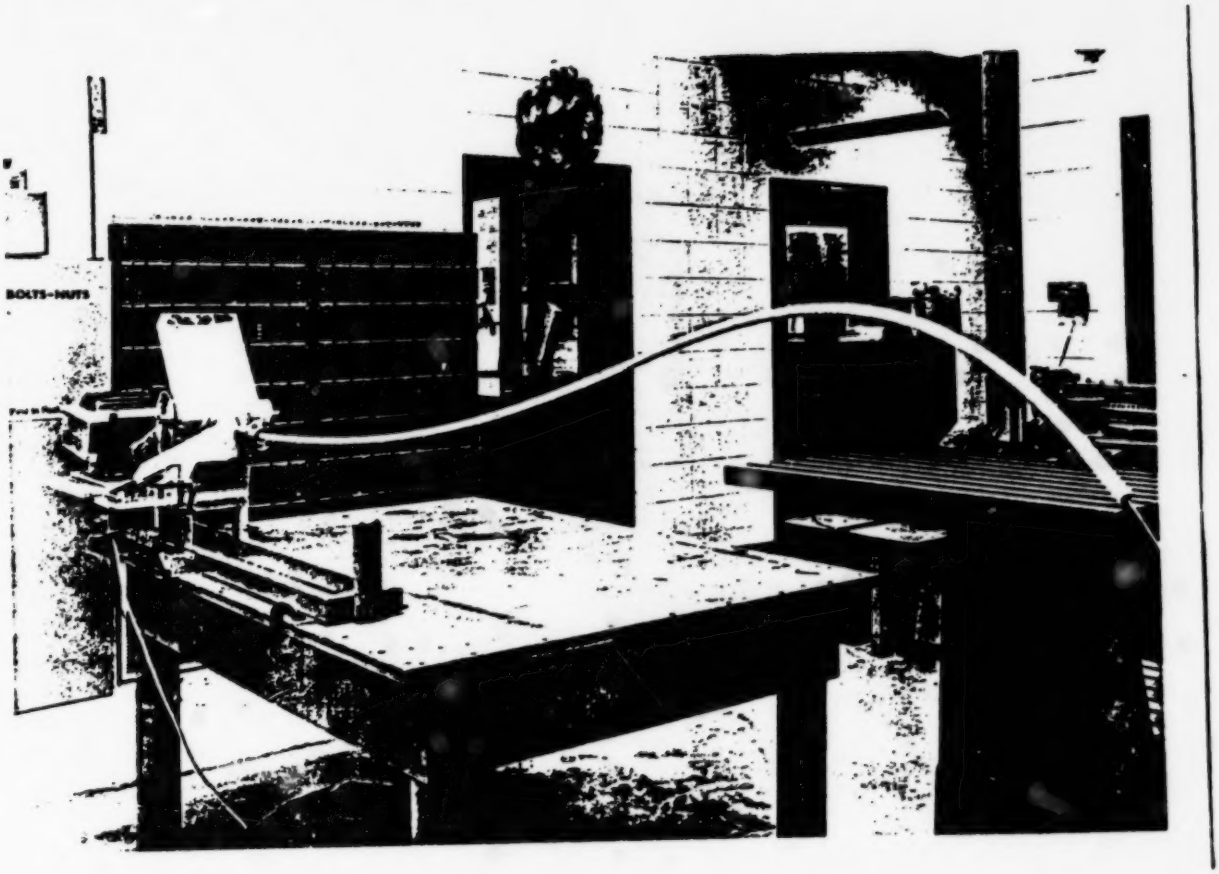

FIG. 3. EXTRUDED WOOD MEAL SPIRAL LEAVING FEEDER

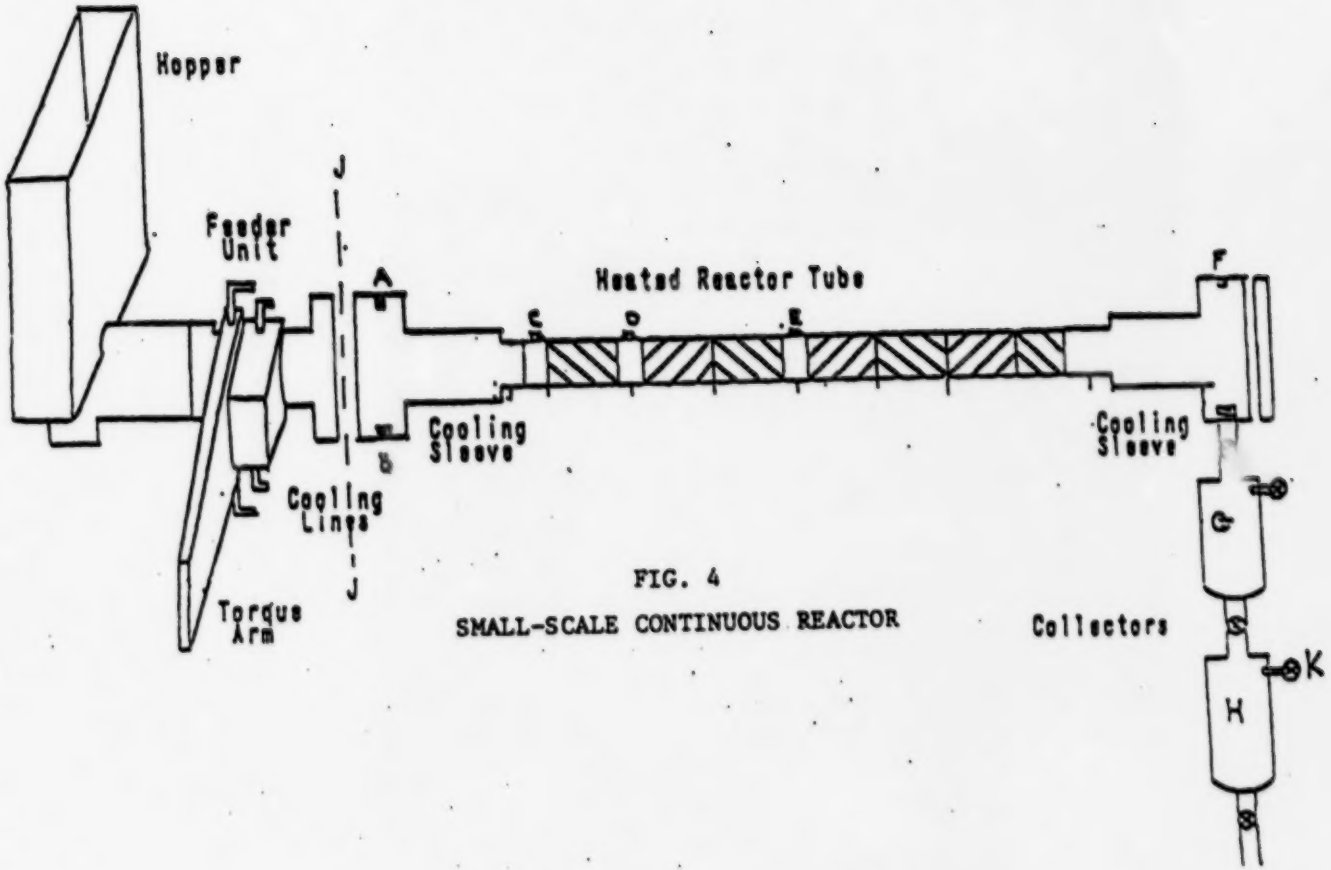

FIG. 4

SMALL-SCALE CONTINUOUS REACTOR

POOR

QUALITY

ORIGINAL